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SYNTHESIS OF FLAME RETARDANT DYE AND ITS APPLICATIONON SILK FABRIC

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ABSTRACT

Nitrogenous based flame retardant enhances the formation of char and quenches fuel, thereby giving flame retardancy to the fabric. Melamine is a flame retardant and also it can be easily diazotized to form a dye. The idea of this project is to couple cyanuric chloride (again a nitrogenous based compound) with melamine thereby, increasing the nitrogen content in melamine and then diazotizing it to form a flame-retardant dye.

In this project, a dye has been synthesized using the two-nitrogen based reactant and its affinity for silk fabric is studied. The detailed dye synthesis is discussed, optimization of dyeing temperature and pH is carried out successfully along with LOI and Vertical Flammability testing.

KEYWORDS: Flame Retardant, Synthesis & Silk Fabric

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Original Article

1. INTRODUCTION

Flame retardants refer to a variety of substances that are added to combustible materials to prevent fires from starting or to slow the spread of fire and provide additional escape time.

The ease of flammability of textiles has been faced by designing and synthesizing suitable flame retardants (FRs), i.e., additives that are able to suppress or delay the appearance of a flame and/or reducing the flame-spread rate (flame retardants) or delaying ignition or reducing the rate of combustion when needed (fire retardants) [2]. Therefore, a pile fabric made from rayon fibers is considered to be highly flammable while a tightly woven fabric made from high twist yarns easily passes the 45^0 (angle) ignition test. Neither however, pass the vertical ignition test. [4]

Thermoplastic fibers present another anomaly - certain fabrics do not ignite when tested by the vertical test, the fabric melts and shrinks away from the heat source. Other fabrics made from the same fiber ignite and fail the test because the fabric construction prevents the rapid withdrawal of the melt from the flame. And finally, there are some fibers which will not ignite at all, they will however char. [4]

Phosphorus and nitrogenous based flame retardants are quite versatile in their flame-retardant action. Phosphorus and nitrogen also work in the condensed phase. Nitrogen alone is not an effective flame retardant; however, it acts synergistically with phosphorous. It is thought that nitrogen reacts with phosphorous to form polymeric species containing P-N bonds. Nitrogen enhances the electrophilicity of phosphorous thereby making it a stronger Lewis acid and also promoting the phosphorylation reaction with the C (6) hydroxyl of the anhydroglucose ring. [4]

2. PURPOSE AND OBJECTIVE

The purpose of the project is to develop a new nitrogenous based flame retardant which canact like a dye. Generally, flame retardants are applied on textile as finishes. The purpose is tomake a chemical which will be flame retardant but will not be superficial like finishes. The advantage of flame retardant dye over flame retardant finishes will be as follows,

- Minimizations of cost: - The cost is expected to decrease as the dyeing and finishing process need not be carried out separately. Both dyeing and flame retardancy can beachieved in a single dyeing process.
- Resistant to washing: - Finishes are superficial and tend to get washed off during washing. However, a dye is more strongly bound to the Fibre through hydrogen bonding, van der Waal's forces or covalent bonding in some cases. This makes the dyeto be more resistant to washing as compared to finishes.
- Feel of the fabric: - Finishes mostly gives a rough feel to the fabric, it also might give tonal variation in the dye and sometimes can also give a foul odor. A dye as it directlybinds with the Fibre can resolve all the above problems and cut down the cost of eliminating such issues.

Experimental Data

Dye synthesis

Three major reactions were carried out under this part namely

- Preparation of Super melamine
- Diazotization of Super melamine using benzene sulphonic acid as a coupler (dye)
- Diazotization of Super melamine using 2- Naphthol as coupler (dye)

3. MATERIALS AND METHODOLOGY

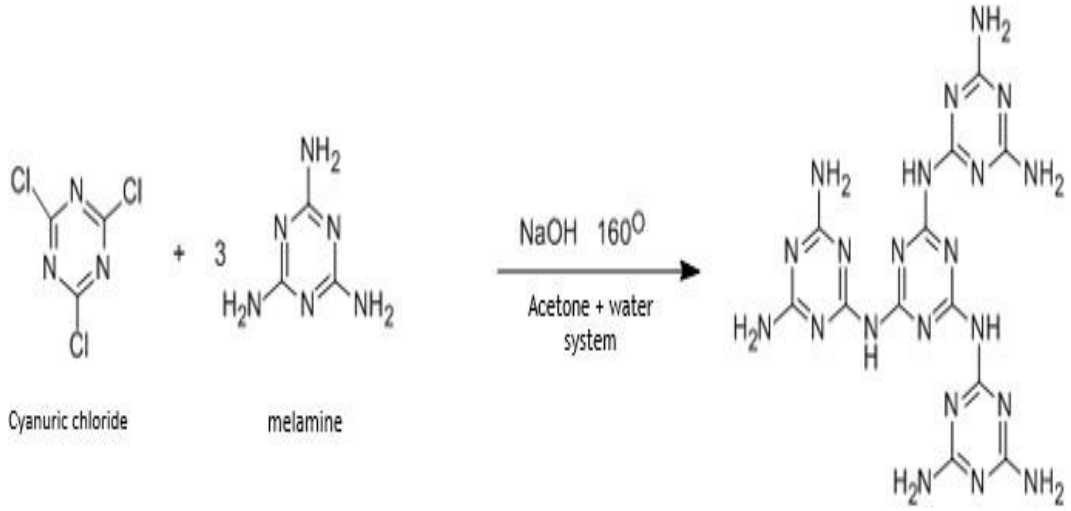
Chemicals

- **Melamine**
- **Cyanuric Chloride**

  Other chemicals used are
- NaOH
- Benzene sulphonic acid
- 2-Naphthol

  The dye is prepared by diazotizing the amine group and coupling it with a suitable solvent.

Synthesis of Super Melamine (dye precursor)



Purpose – To increase nitrogenous based groups in melamine. As it will enhance the formation of char and quench the fuels from the fire making fabric flame retardant. Also, the amino groups can diazotize forming some suitable azo dyes.

Procedure

Table 1: Equivalence of Reactant for the Reaction

Sr. No.	Compound	Molar Mass (g/mol)	AmountTaken (g)	mmol	Equivalent
1	Melamine	126.123	0.411	3.255	3
2	Cyanuric chloride	184.400	0.200	1.085	1
3	NaOH	39.397	0.087	2.`70	2

Reaction Code – Super Melamine

- Cyanuric chloride was added in RB flask along with 20 ml of acetone
- NaOH was then added – colour changed from colorless to yellow on stirring
- 5 ml of water was added to decrease vaporization of acetone.
- Melamine was added to the RB flask
- The temperature was raised to 160 degrees within a span of 20min.
- A yellow colour ppt is and no further changes is observed.
- The reaction completes after 90 min.
- TLC of compound shows no spots due to poor solubility.

Figure 1: TLC for Super Melamine.

Spots from left to right

- Melamine (water)
- Cyanuric chloride (acetone)
- Co-spot
- Super melamine (DMSO) – No spot was seen
    - Hence the compound was allowed to cool down. It was filtered and washed several times with water and acetone.
    - The residue is our compound which is dried and weighed to be 0.113g.
    - The filtrate was also Rota dried to obtain a white solid.
    - The residue was light yellow in colour and was soluble in DMSO after sonicating.
    - The residue was not soluble in water, ethanol, methanol, chloroform, ethyl acetate,toluene, acetonitrile, DMF

The IR of the compound was taken.

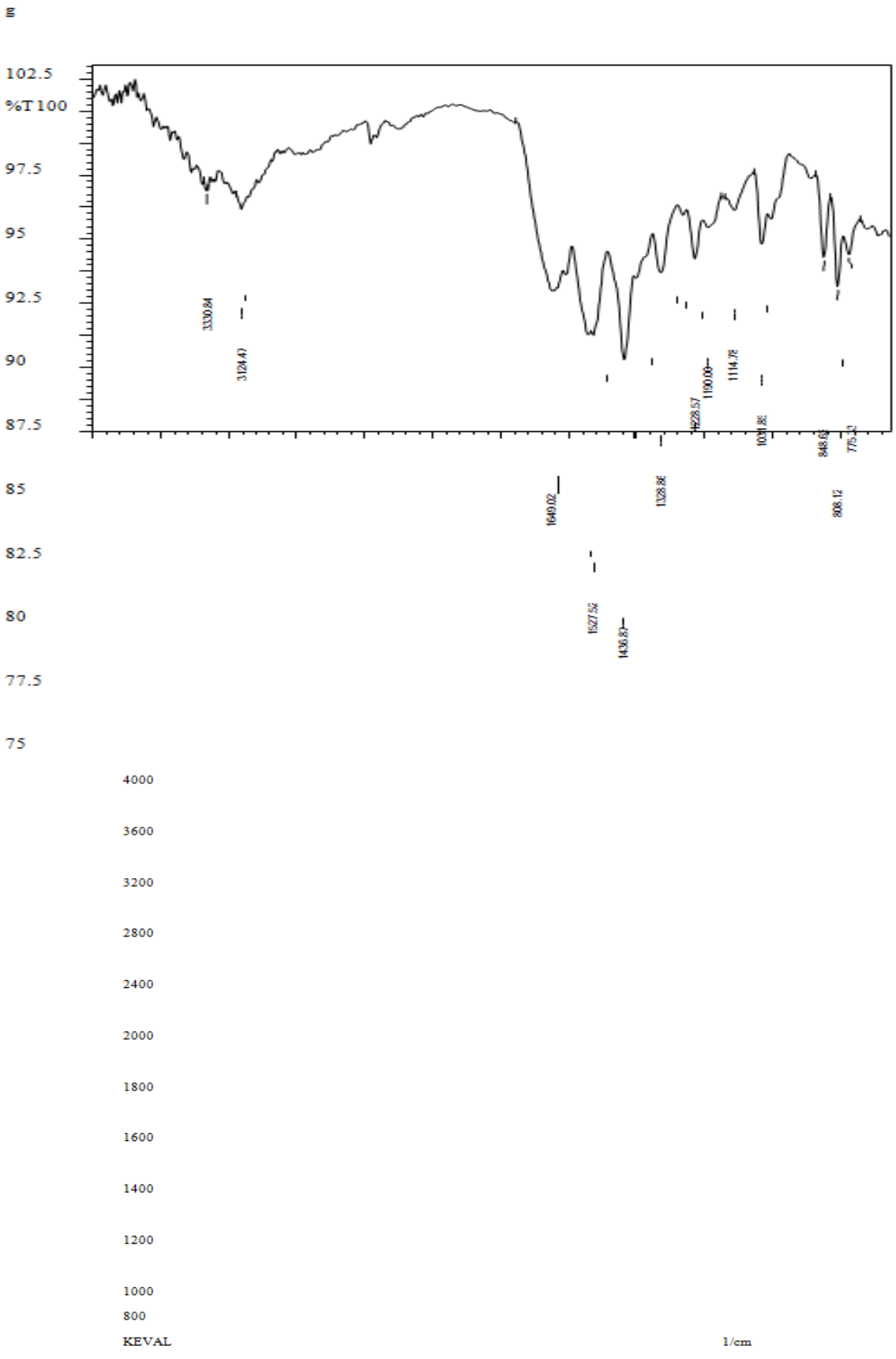


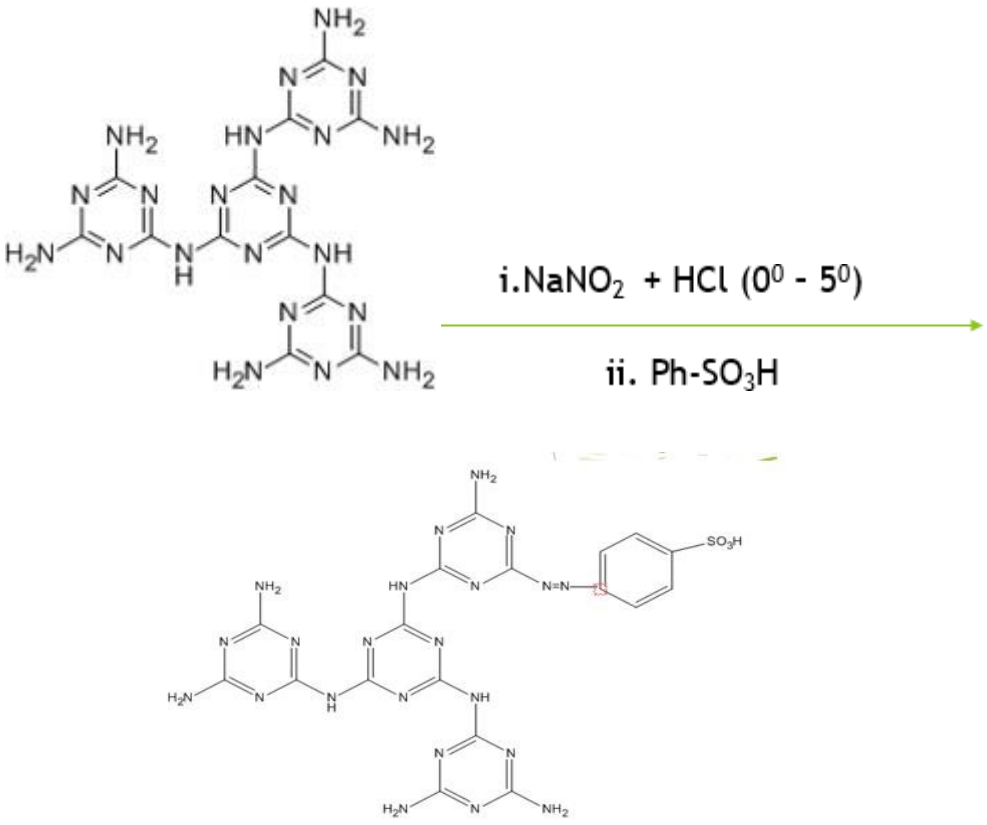
Figure 2: IR Graph for Super Melamine.

- The sharp peak 1436.87 indicates bending by C-H bond
- The strong two bands at 1527.52 indicates N-O group stretching
- The medium weak peak at 1328.86 indicates C-N stretching
- The broad peak at 1649.02 indicates N-H bending
- The band at 1287.57 indicates C-H stretching
- The sharp band at 800 and near indicates =C-H bending.

Diazotization of Super Melamine

Diazotization of super melamine was carried out using two different couplers and two dyeswere synthesized

Part A: Diazotization and coupling with benzene sulphonic acid



Diazotization and Coupling Procedure

- 0.5 g of super melamine was added in a round bottom flask.
- 1:1 ratio of HCl and water was mixed in a test tube and was cooled in an ice bath.
- The cold solution was added to RB containing substrate which was kept in an icebath.
- The addition was done roughly till all the substrate was dissolved completely.

- 1% $NaNO_2$ solution was prepared separately and was added to RB slowly so thatthe exotherm do not raise the temperature beyond 5°c
- The solution had a lot of bubbles formation at this time.
- It was allowed to sit for 40 min with temperature being controlled and withcontinuous stirring.
- After this point, the diazotised super melamine was distributed in two parts andwere coupled using different couplers

- **Part A**: 5ml of benzene sulfonic acid was added dropwise till the solution changed from pale yellow to dark yellow then to brown (colour of benzene sulfonic acid).

The compound was water soluble hence no precipitate was formed. The compound was Rota dried and was directly used for dyeing.

- **Part B** – Coupled with 2-Naphthol
- 2-Naphthol was dissolved in alkaline water.
- This solution of 2-Naphthol was slowly added in the diazotised mixture and aprecipitate was obtained.
- Excess of coupler is added so that all the diazotised super melamine reacts with 2-naphthol and the excess of 2-Naphthol becomes insoluble.
- The solution was filtered and washed with water.
- Filtrate was collected and solvent extraction using DCM was carried out severaltimes.
- Most of the dye was extracted by solvent however some remained in water.
- The dye in DCM was Rota dried.
- The dye was not completely pure however it was free from the dark brown colourof 2-naphthol.
- The dye had pale yellow colour and was used for further dyeing.
- The dye that remained in water was dark yellow in colour however when dried completely was a brown solid indicating the dye had retained 2-naphthol in it.

Figure 3: Dye with Phenyl Sulphonic Acid

Figure 4: Stock Solution of Dye with 2-Naphthol Separated after Solvent Extraction.

Figure 5: Impure Dye with 2-Naphthol Containing Excess of 2-Naphthol.
Figure 6: TLC of Dye with 2-Naphthol (Solution in figure7)

Dyeing

As two dyes were synthesized, for further referencesD1 – Dye with benzene sulphonic acid

D2 – Dye with 2-naphthol

Materials and Machine

- Substrate- Silk fabric
- Non-Ionic soap for washing (Celldet R)
- Glacial acetic acid
- Soda ash
- pH paper
- Rota dyer for dyeing (dye fixation)
- Spectrophotometer
- IR machine
- Vertical flame-retardant machine
- LOI testing machine

Optimization of Dyeing Conditions

Cotton was initially dyed but it gave no result hence dyeing was done on silk.

Optimization of pH

Procedure

- The silk fabric was first washed with a non-ionic soap for 30 min to remove any finishfrom it.
- Silk was dyed with 1% shade in Rota dyer with both the dyes D1 and D2 at 90^0c for 60min at three different pH i.e. 3,5 and 7.

- The dye solution taken was owf.
- M: L ratio was 1:50
- No auxiliaries were added
- pH 3 was maintained by acetic acid solution
- pH 7 was maintained by soda ash solution
- PH was determined by pH paper
- The K/S values were calculated which are as follows

Table 2: K/S Value for Optimization of pH

Substrate with Dye	pH	K/S	Strength (%)
Standard silk	-	0.582	100.000
D1	**3**	**1.756**	**301.718**
D1	5	1.138	195.533
D1	7	0.968	166.323
D2	**3**	**1.153**	**198.110**
D2	5	1.013	174.055
D2	7	0.882	151.546

Conclusion- pH 3 was the best pH to dye silk with both the dyes.Optimization of Temperature

Similar procedure was carried out but this time the pH was kept constant at 3 using aceticacid and temperature were varied for 60^0c, 75^0c and 90^oc.

The K/S values were recorded which were as follows

Table 3: K/S value for Optimizations of Temperature

Substrate with dye	Temperature (^{0}c)	K/S	Strength (%)
Standard silk	-	0.582	100.000
D1	60	0.813	139.691
D1	75	1.290	221.650
D1	**90**	**1.756**	**301.718**
D2	60	0.775	133.162
D2	75	1.064	182.818
D2	**90**	**1.153**	**198.110**

Conclusion- 90^oc was observed to be the best temperature of dyeing for silk with both thedyes

Flame Retardancy and its Testing

Limiting Oxygen Index

Limiting oxygen index (LOI), also called oxygen index (LOI), is one of the most popular scientific methods, used in many standards, such as ISO 4589 and ASTM D2863. LOI denotes the minimum concentration (vol %) of O2 in a mixture of O2 and N2 that will just sustain flamingcombustion of a material in a candle-like manner. Textile materials burn rapidly when

they exhibit LOI values up to 21 vol %, while they burn slowly when LOI is in between 21 vol % and25 vol %. LOI values **beyond 26 vol % indicate some flame-retardant features.** [4]

The obtained LOI values may be affected by several fabric structural parameters, when measured for the same fiber type: this makes LOI values relative and not absolute data. In addition, the textile material is ignited at the top and thus it burns vertically downward (i.e., in candle-like manner) which is opposite to the burning of any material freely suspended. [4]

Vertical Flammability and Char Length

A sample of 12 x 30 cm is placed in the vertical flammability tester. The fabric is allowed to burn for 12 seconds. The char length is measured. A flame retardant must have the least possible char length.

Most organic fibers undergo a glowing action after the flame has been extinguished, and flame-resistant fabrics should also be glow resistant. Afterglow may cause as much damage as the flaming itself since it can completely consume the fabric. The burning (decomposition)temperature of cellulose is about 230 degrees C, whereas afterglow temperature is approximately 345 degrees C. [11]

The fabric was dyed at different % shade and was washed. The LOI and char length was measured for both washed and unwashed fabric.

Dyeing and Soaping for LOI

- For LOI testing, a 6 x 9 cm of fabric was dyed with D1 (Benzene sulphonic acid) in threedifferent shades which were 1%, 2% and 3%.
- Along with that 6 x 9 cm fabric was dyed with D2 (2-naphthol) in two different shadeswhich were 1% and 2%.
- Dyeing was carried out in Rota dyer at 90^{o}c at a pH 3. The pH was maintained by glacialacetic acid.
- No other auxiliaries were added. The M: L ratio was maintained as 1:50.
- After dyeing the fabric were air dried and some of the samples were washed usinga non-ionic detergent at 60^{0}c for 30 min.
- The washed sample were air dried and were checked for LOI.In all the images below from left to right-
    - Undyed silk
    - Dyed silk
    - Dyed and washed silk

Figure 7: Dyed with 1% Shade with Dye-2.

Figure 8: Dyed with 2% shade with Dye-2.

Figure 9: Dyed with 2% shade with Dye-1.

Figure 10: Dyed with 3% shade with Dye-1.

The LOI values were as follows

Table 4: LOI Results for Dyed and Washed Silk Fabric

Sr. No.	Dye	% Shade	LOI (Before Wash)	LOI (After Wash)
1	Undyed Silk	-	18%	18%
2	Dye-2 (2-naphthol)	1%	21%	20%
3	Dye-2 (2-naphthol)	2%	22%	20%
4	Dye-1 ($PhSO_3H$)	1%	21%	20%
5	Dye-1 ($PhSO_3H$)	2%	22%	21%
6	Dye-1 ($PhSO_3H$)	3%	23%	22%

Observations

The compound shows flame retardancy but it is not enough to call the dyed fabric flameretardant as all LOI are below 26%.

As the concentration of dye in fabric increases flame retardant character also increasesDye has poor wash fastness as the colour difference is very much visible.

Dyeing and Soaping for Vertical Flammability Testing

- For vertical flammability testing, a 12 x 30 cm of fabric was dyed with D1 (Benzenesulphonic acid) in three different shades which were 1%, 1.5% and 2%.
- Dyeing was carried out in Rota dyer at 90^{o} c at a pH 3. The pH was maintained by glacialacetic acid.
- No other auxiliaries were added. The M: L ratio was maintained as 1:50.
- After dyeing the fabric were air dried and some of the samples were washed usinga non-ionic detergent at 60^{0}c for 30 min.
- The washed sample were air dried and were checked for LOI.

In all the images below from left to right-

- Unwashed 1%
- Unwashed 1.5%
- Unwashed 2%

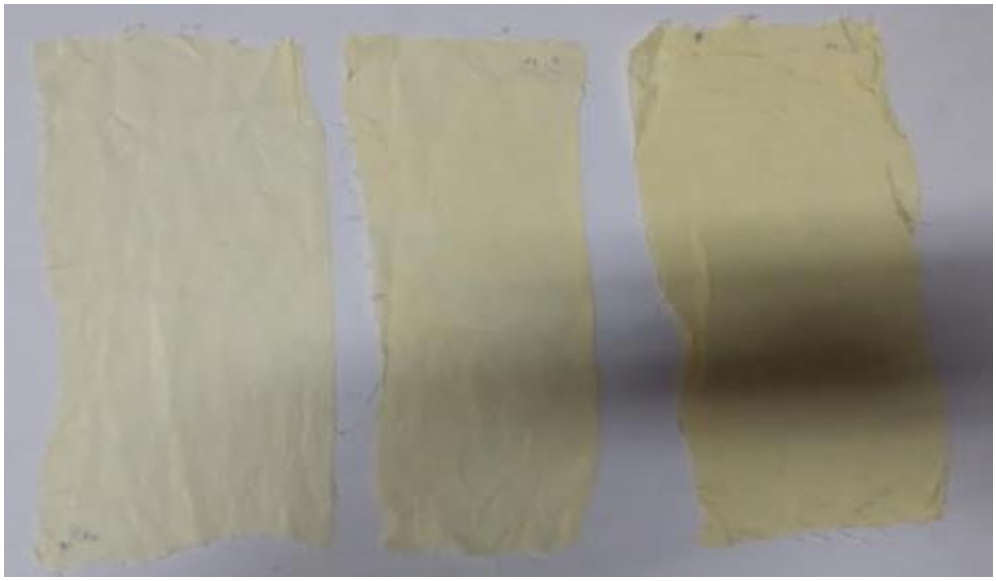


Figure 11: Shade variation in Silk, Dyed with Dye-1.

The vertical flammability testing of dyed (with Dye-1) and washed fabric was done and theresults were as follows:

Table 5: Char Length Results for Dyed and Washed Silk Fabric

Sr. No.	% Shade	Char Length (before Washing)	Char Length (after Washing)
1	Undyed	25.2 cm	25.2 cm
2	1.0%	16.2 cm	18.3 cm
3	1.5%	12.7 cm	21.8 cm
4	**2.0%**	**10.7 cm**	23.2 cm

In all the images below from left to right-

- Undyed silk
- Dyed silk
- Dyed and washed silk

Figure 12: Char length for 1% shade of Dye-1.

Figure 13: Char Length for 1.5% shade of Dye-1.

Figure 14: Char Length for 2% Shade of Dye-1.

Observation

As the concentration of dye in fabric increases flame retardant character also increases However, the char length values are too high and the dyed fabric cannot be called as fireretardant

4. CONCLUSIONS AND DISCUSSION

The char length value is greater due to which the dyed fabric cannot be called as flameretardant. However, it is observed that flame retardancy increases with increase in concentration of super melamine (for both dyes). Thus, it can be concluded that the dyes prepared has some flame-retardant properties but the property has to be needs enhanced.

The dye prepared has extremely poor washing fastness. The reason for it can be high solubility of dye in water which makes it easier to dye but also shows poor fastness property.This drawback can be studied again by purifying the dye completely and then checking its solubility. As of now, the dye synthesized cannot be called as a dye as it shows extremely poorwash fastness.

The above two conclusions, tempt me to think that the compounds synthesized must be checked for an auxiliary in silk dyeing rather than an actual dye. Even in that case dyeing and flame retardancy would be achieved in a single step rather than the conventional twostep process. The advantage of it, to be used as an auxiliary will be that its concentration in dyeing can be increased up to 10%. Higher the concentration higher will be the flame retardancy as this is clearly observed in this project.

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